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Methanol to Aromatics on Hybrid Structure Zeolite Catalysts

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Abstract: A study on the reaction of methanol to aromatic hydrocarbons using catalysts based on hybrid zeolites MFI-MEL, MFI-MTW, and MFI-MCM-41 at a temperature of 340 °C and a pressure of 10.0 MPa was carried out. It is shown that in the synthesis of hydrocarbons under pressure, the activity of the studied samples is similar and does not have a linear correlation with their total acidity. It was found that the catalyst's activity is primarily determined by the rate of the initial methanol conversion reaction, which is related to the volume of micropores—more micropores lead to higher activity. Additionally, increasing the volume of mesopores results in the formation of heavier aromatic compounds, specifically C_{10}–C_{11}.

Keywords: methanol to aromatics; hybrid zeolites; intergrowth structure; MEL; MTW; MCM-41; MFI

1. Introduction

The process of converting methanol into hydrocarbons on a zeolite catalyst, referred to as the MTG (Methanol to Gasoline) process, has been known since the second half of the 20th century. However, with the advancement of decarbonization in the petrochemical industry and the development of methanol synthesis technologies using CO_2 as a reagent, research into the process of synthesizing hydrocarbons from methanol remains relevant.

In the synthesis of hydrocarbons from oxygenates, a catalyst based on the MFI zeolite structure is most commonly used. The most well-known industrial brand of this zeolite is ZSM-5 (Zeolite Socony Mobil–5) from Mobil (Spring, TX, USA). It is characterized by high productivity for liquid hydrocarbons and a low deactivation rate. Until 2010, the most common methods for modifying the catalyst were its promotion with various metals and zeolite desilication/dealumination. For instance, the introduction of Ga, Zn, and Ag into the catalyst increases the yield of aromatic compounds [1,2]. Desilication/dealumination leads to the formation of randomly oriented mesopores surrounded by micropores, which slightly extends the catalyst's lifetime and increases the propylene/ethylene ratio due to its open mesoporosity [3].

Currently, alternative zeolite structures such as zeolites with a two-dimensional channel structure (MEL) or a one-dimensional channel structure (MTW) are being considered for the synthesis of hydrocarbons from oxygenates [4–6]. For example, in [7], it has been shown that the MEL zeolite can compete with MFI zeolite in terms of catalyst deactivation rate and propylene selectivity (35% versus 27%). Catalysts based on the MTW zeolite structure are also a good alternative to traditional zeolites in terms of propylene and butene formation, with a combined yield reaching 65 mol% C [8].

Additionally, to increase the yield of target products, the synthesis of zeolites with a hybrid structure, by combining different zeolite structures such as MFI and MEL, MFI and MTW, MFI and BEA, MFI and AEL, and MFI and FER, is actively being developed.

Hybrid materials can be obtained through the co-crystallization of zeolites with different structures or in the synthesis of "core-shell" type structures [9–14]. For example, in [11], samples based on the MFI/MTW structure were synthesized by various methods. It has been shown that compared to the standard MFI-based sample, these samples exhibit high selectivity for lower olefins (28% versus 19%) with a high proportion of propylene in the product (propylene/ethylene ratio of 0.79 versus 0.58) during methanol conversion. High results were also achieved with the hybrid co-crystallized MFI/MEL zeolite, which showed a 47% propylene formation selectivity at 100% methanol conversion, compared to 27% for MFI zeolite [9].

In a previous study [15], we investigated catalyst samples based on co-crystallized MFI-MEL, MFI-MTW, and "core-shell" MFI-MCM-41 structures in the reaction of synthesizing olefins from dimethyl ether (DME). It has been shown that at high DME conversions for catalysts based on MFI and MFI-MEL zeolites, the molar ratios of ethylene/propylene are close and range from 1.1 to 1.2. For the MFI-MTW-based catalyst, the lowest ethylene/propylene ratio of 0.8 was observed, while the "core-shell" MFI-MCM-41 structure showed the highest ratio of 1.45. It was suggested that under atmospheric pressure, the presence of micropores influences the selectivity of product formation, particularly ethylene, by stabilizing key intermediates like alkylcyclopentyl cations and polymethyl-substituted aromatic hydrocarbons. Moreover, it was shown that the topology of the hybrid zeolite determines the hydrogen transfer reaction rates but does not affect the isomerization activity of the catalyst. The next step in the research is to study how the hybrid structure of zeolites influences the synthesis of liquid hydrocarbons, particularly aromatic compounds, under increased pressure. The aim of this study is to establish the relationship between the physicochemical characteristics of the zeolite component of the catalyst and the composition of the resulting gaseous and liquid products in the reaction of methanol conversion to hydrocarbons at elevated pressure.

2. Results and Discussion

Under the conditions of catalyst testing, T = 340 °C and P = 10.0 MPa, methanol conversion increases in the following order: MFI-MTW/Al_2O_3 < MFI-MCM-41/Al_2O_3 < MFI/Al_2O_3 < MFI-MEL/Al_2O_3 (Figure 1a). For the three samples based on MFI, MFI-MEL, and MFI-MCM-41 zeolites, the pattern of methanol conversion on contact time can be described by a single dependence (Figure 1b).
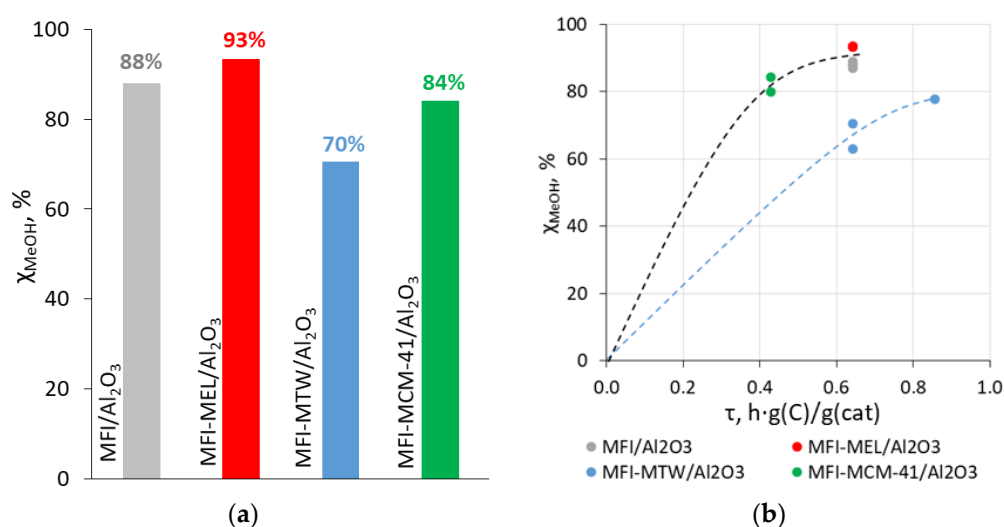

Figure 1. (**a**) Methanol conversion on hybrid zeolite catalysts. (**b**) Dependence of methanol conversion on specified contact time. T = 340 °C, P = 10.0 MPa.

When testing these catalysts in the reaction of converting dimethyl ether to lower olefins at atmospheric pressure, we observed a linear correlation between the activity of the samples and their total acidity: the MFI/Al$_2$O$_3$ sample, with a total acidity of 495 μmol NH$_3$/g(cat)×h, demonstrated the highest activity, while the MFI-MTW/Al$_2$O$_3$ sample, with a total acidity of 266 μmol NH$_3$/g(cat)×h, showed the lowest activity [15]. However, such a correlation was not observed when the reaction was conducted under pressure. The observed effect can be explained by the decrease in the mean free path as pressure increases, which results in a shift diffusion from Knudsen to Fickian. Since the Fickian diffusion coefficient is inversely proportional to pressure, increasing the pressure to 10 MPa significantly reduces the diffusion coefficient [16,17]. Consequently, under increased pressure, the observed reaction rate is mainly determined by internal diffusion. Although the intrinsic reaction rate increases with the catalyst's acidity, this is not observable due to the limiting diffusion constraints. Therefore, the observed reaction rate under increased pressure is determined by the total volume of micropores, where the primary reactions of the MTO process occur. Therefore, a correlation was observed: with an increase in the volume of micropores of the catalyst, its activity increases (Table 1, Supplementary Materials: Figure S6).

Table 1. Product yields of the methanol-to-hydrocarbon reaction on hybrid zeolite catalysts.

	MFI/Al$_2$O$_3$	MFI-MEL/Al$_2$O$_3$	MFI-MTW/Al$_2$O$_3$	MFI-MCM-41/Al$_2$O$_3$
Micropore volume, cm^3/g	0.057	0.088	0.012	0.04
Micropore diameter, nm	0.9	0.91	0.69	0.63
Mesopore volume, cm^3/g	0.142	0.198	0.431	0.300
Mesopore diameter, nm	8.27	5.79	19.67	7.58
Yield, wt.C%:				
DME	0.4	0.4	15.1	0.5
Lower olefins C$_2$–C$_4$	0.2	0.6	3.1	0.5
Gaseous hydrocarbons C$_1$–C$_4$	35.7	24.3	18.8	26.6
Liquid hydrocarbons C$_5$–C$_{11}$	36.2	52.4	34.6	54.3
Mass ratio gas/liquid	1.0	0.5	0.6	0.5

The confirmation of the proposed relationship between the catalyst activity and micropore volume is the high yield of dimethyl ether (15.1 wt.C%) and the presence of lower olefins C$_2$–C$_4$ (yield = 3.1 wt.C%) in the gas phase on the MFI-MTW/Al$_2$O$_3$ catalyst with the smallest volume of micropores (Table 1, Figure 2).
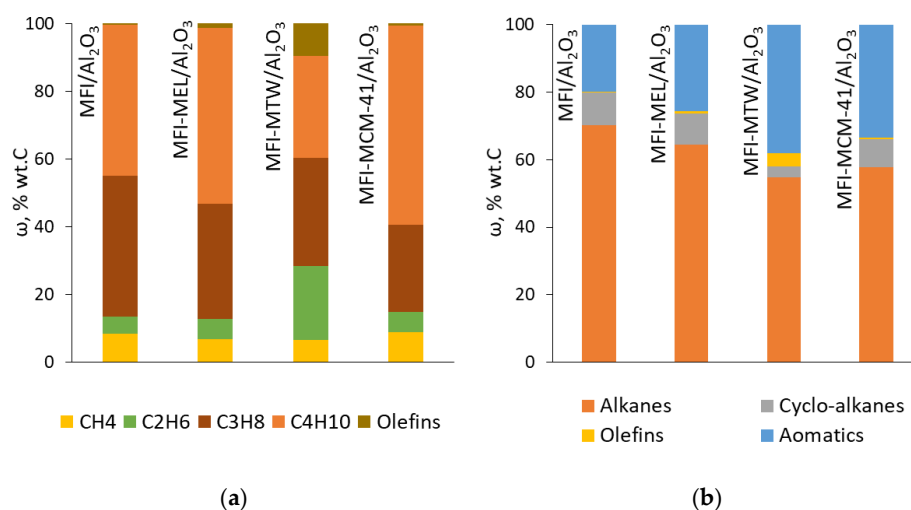

(a) (b)

Figure 2. Distribution of individual compounds in methanol conversion on hybrid zeolite catalysts. (**a**) gaseous hydrocarbons C$_1$–C$_4$; (**b**) liquid hydrocarbons C$_5$–C$_{11}$.

The gaseous hydrocarbons C_1–C_4 for the MFI/Al_2O_3, MFI-MEL/Al_2O_3, and MFI-MCM-41/Al_2O_3 catalysts were mainly composed of propane and butanes, with a total proportion exceeding 80 wt.% (Figure 2). For the MFI-MTW/Al_2O_3 catalyst, a significant amount of olefins C_2–C_4 (9.5 wt.%) was present among the gaseous hydrocarbons, directly confirming the primary formation of lower olefins in the synthesis of liquid hydrocarbons.

For the MFI/Al_2O_3, MFI-MEL/Al_2O_3, and MFI-MCM-41/Al_2O_3 catalysts, the major constituent of the liquid phase was isoalkanes C_5–C_{11}, comprising 52 to 66 wt%. The highest content of aromatic hydrocarbons was observed for MFI-MTW/Al_2O_3 at 38.2 wt.%.

For the MFI/Al_2O_3 and MFI-MEL/Al_2O_3 samples, within the aromatic compounds, the predominant constituents were C_9–C_{10} compounds, with their total share reaching 72–75 wt%. (Figure 3). For the MFI-MTW/Al_2O_3 and MFI-MCM-41/Al_2O_3 catalysts, the focus shifted towards the formation of C_{10}–C_{11} aromatic hydrocarbons (Figure 3, Supplementary Materials: Figure S7). This can be linked to the volume of mesopores in the catalyst, which was 0.142 and 0.198 cm^3/g for MFI/Al_2O_3 and MFI-MEL/Al_2O_3, respectively, and 0.431 and 0.300 cm^3/g for MFI-MTW/Al_2O_3 and MFI-MCM-41/Al_2O_3, respectively. The increased volume of mesopores in catalysts based on hybrid zeolite promotes the release of bulky aromatic compounds from the zeolite pores into the gas phase. Consequently, we can make another important conclusion linking the textural characteristics of the catalytic material and the distribution of reaction products: the larger the volume of mesopores in the catalyst structure, the faster the hydrogen transfer reactions, leading predominantly to the formation of aromatic compounds.
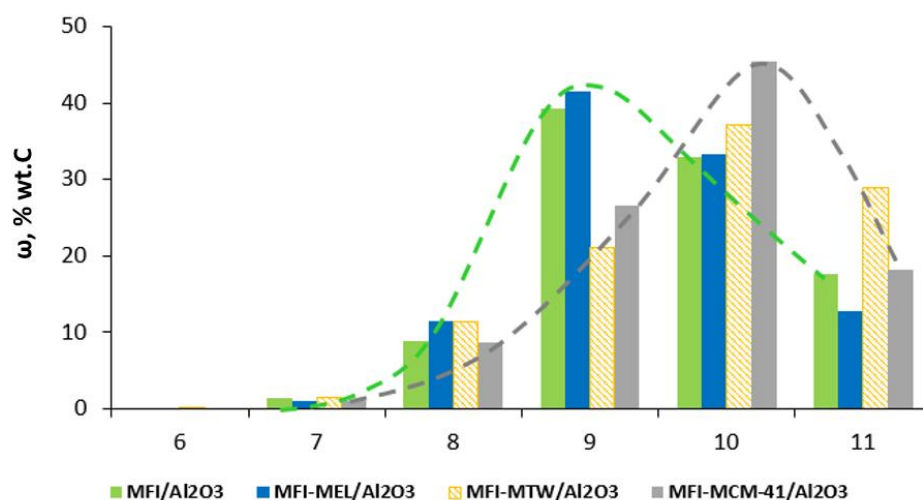

Figure 3. Distribution of individual aromatic compounds in methanol conversion on hybrid zeolite catalysts. Green dotted line: interpolation for MFI/Al_2O_3 and MFI-MEL/Al_2O_3, grey dotted line: interpolation for MFI-MCM-41/Al_2O_3.

3. Experimental Section

3.1. Zeolite Synthesis

The MFI zeolite and hybrid co-crystallized zeolites (MFI-MEL, MFI-MTW, MFI-MCM-41) were synthesized at the Department of Chemistry, Moscow State University [15]. Detailed studies on the physicochemical properties of zeolites and catalysts based on were conducted in [15] and the patents [18,19]. The most important physicochemical properties of zeolites and catalysts are presented in the Supplementary Materials (Supplementary Materials: Tables S1–S4, Figures S1–S5). The Si/Al ratio for the standard MFI-based sample is 48; for the hybrid zeolite samples (MFI-MEL, MFI-MTW, MFI-MCM-41), the ratios are similar, ranging from 53 to 55. The phase ratios in the hybrid zeolites are as follows: MFI-MEL = 55/45 wt.%, MFI-MTW = 60/40 wt.%, and MFI-MCM-41 = 80/20 wt.%.

3.2. Catalyst Preparation

42.7 g of AlO(OH) were placed in a mixer and 20 mL of a peptizing solution (5 mL of 1.0 M aqueous HNO_3 + 15 mL of H_2O) was added. The mixture was stirred for 5 min. Then, 76.5 g of dry zeolite was added. The mass was stirred for 20 min at 60 °C. After that, the catalytic mass was passed through an extruder with a die diameter of 2.5 mm. The extrudates are dried in an oven at 80 °C, 90 °C, 100 °C, 110 °C, and 120 °C for 3 h at each temperature, then calcined in a muffle furnace at 550 °C for 7 h. During calcination, AlO(OH) is converted to Al_2O_3. The final content of Al_2O_3 in the material obtained was 30 wt%.

3.3. Experimental Procedure

The experimental unit for the synthesis of liquid hydrocarbons from methanol has been described in several of our works, such as [20,21]. The methanol-to-hydrocarbon conversion was carried out in a flow-circulation mode at a pressure of 10.0 MPa and a temperature of 340 °C, using hydrogen as a carrier gas at a flow rate of 5 L/h. The reactor was loaded with 2–3 g of catalyst. Methanol was fed into the system using a dosing pump at a rate of 6 mL/h. The circulating gas flow rate was 180–185 L/h, with a vent gas flow rate of 5 L/h.

Liquid reaction products (organic and aqueous phases) were collected after 24 h of operation, and their quantity and composition were analyzed. The volume of dissolved gases in the liquid phase was determined using a special burette. The composition of the liquid phase, vent gases, and degassing products was determined chromatographically.

For each experiment, a material balance was calculated based on the composition and quantity of the resulting products. The analysis of the gas phase (C_1–C_5) was performed using a Chrom-5 gas chromatograph (Laboratory Instruments, Prague, Czech Republic) with a combined packed column containing the sorbent Polysorb 1, modified with Carbowax 3000, a flame ionization detector, and the carrier gas was helium, and the column temperature was programmed to rise from 50 to 180 °C.

The composition of the liquid organic phase was analyzed using a Crystallux 4000M chromatograph (Production Company Meta-Chrom, Yoshkar-Ola, Russia) with a flame ionization detector and a capillary column with a non-polar phase Petrocol (100 m × 0.325 mm × 0.5 µm) in a temperature-programmed mode (35–250 °C, heating rate 2 °C/min), with helium as the carrier gas (flow rate 2 mL/min).

3.4. Data Processing

The main indicators used to evaluate the process were methanol conversion, the product yields based on carbon, and the distribution of individual components or groups.

Methanol conversion was calculated using the following formula:

$$X_{MeOH} = \frac{m_{\text{in}(MeOH)} - m_{\text{out}(MeOH)}}{m_{\text{in}(MeOH)}} \cdot 100, \% \tag{1}$$

where $m_{\text{in}(MeOH)}$ and $m_{\text{out}(MeOH)}$ are the masses of methanol inlet and outlet, respectively, in g/h.

The yield of carbon-containing products was calculated using the following formula:

$$Y_i = \frac{m_{\text{out}}(C)_i}{m(C)_{\text{in}(MeOH)}} \cdot 100, \text{ wt.C\%} \tag{2}$$

where $m_{\text{out}}(C)_i$ is the mass of carbon of the i-th product, in g/h, and $m(C)_{\text{in}(MeOH)}$ is the mass of carbon in the inlet methanol, in g/h.

The yields of gaseous and liquid hydrocarbons were calculated using Equations (3) and (4):

$$Y_{GHC} = \sum_{k=1}^{4} Y_k, \text{ wt.C\%} \tag{3}$$

$$Y_{LHC} = \sum_{k=5}^{11} Y_k, \ \text{wt.C\%} \tag{4}$$

where Y_k is the yield of an individual hydrocarbon, in wt.C%.

The distribution of individual substances and component groups was calculated using the following formula:

$$\omega_i = \frac{m(C)_i}{\sum_i m(C)_i} \cdot 100, \ \text{wt.C\%} \tag{5}$$

where $m(C)_i$ is the mass of carbon in the i-th product, in g/h, and $\sum_i m(C)_i$ is the total mass of carbon in the group, in g/h.

4. Conclusions

The study investigated the conversion of methanol to aromatic hydrocarbons using co-crystallized hybrid zeolite catalytic systems in a flow-circulation reactor unit at a pressure of 10.0 MPa and a temperature of 340 °C.

The results showed that the catalytic systems based on MFI, MFI-MEL, and MFI-MCM-41 zeolites showed similar activity, achieving methanol conversions of 84–94%. The catalyst based on MFI-MTW zeolite showed the lowest activity with a methanol conversion of 70%. For this catalyst, the gaseous hydrocarbons contained dimethyl ether and C_2-C_4 olefins.

It was demonstrated that under increased pressure, the acidic properties of the samples play a secondary role. The activity of the catalyst is mostly determined by the diffusion restrictions and by the total volume of micropores. Therefore, at high pressure, the catalyst activity and the distribution of reaction products are determined by the textural properties of the catalyst: the volume of micropores is responsible for the observed rate of primary MTO-reactions, while the volume of mesopores is responsible for secondary reactions such as H-transfer and aromatization. The use of hybrid co-crystalline zeolites MFI-MCM-41 and MFI-MTW leads to an increase in the content of heavier aromatic compounds in liquid hydrocarbons due to the enlargement of the catalyst's mesopore volume.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal14070461/s1, Table S1: Composition of hybrid zeolites; Figure S1: XRD patterns of the catalysts; Table S2: Textural properties of the catalysts and indexed hierarchy factor of the catalysts [22]; Figure S2: BJH plots (desorption curve) for the catalysts, Figure S3: t-plots for nitrogen adsorbed in the catalysts; Figure S4 NH_3-TPD profiles of the catalysts; Table S3: Acidic properties of catalysts; Figure S5: IR spectra of pyridine adsorbed on hybrid zeolites; Table S4: Acid characteristics of hybrid zeolites; Figure S6: Dependence of methanol conversion on the volume of micropores in the catalyst; Figure S7: Dependence of average number of carbon atoms in aromatic compounds on the volume of mesopores in the catalyst.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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